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<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A61K 47/48, C08G 63/00, C07D 209/20, C07C 235/52</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/06825</b> <b>(43) International Publication Date:</b> 27 February 1997 (27.02.97)									
<b>(21) International Application Number:</b> PCT/US96/13341 <b>(22) International Filing Date:</b> 14 August 1996 (14.08.96)  <b>(30) Priority Data:</b> <table border="0"><tr><td>08/516,853</td><td>18 August 1995 (18.08.95)</td><td>US</td></tr><tr><td>08/516,667</td><td>18 August 1995 (18.08.95)</td><td>US</td></tr><tr><td>08/516,587</td><td>18 August 1995 (18.08.95)</td><td>US</td></tr></table> <b>(71) Applicant:</b> HOECHST CELANESE CORPORATION [US/US]; Route 202-206, Somerville, NJ 08876 (US).  <b>(72) Inventors:</b> JUNEAU, Kathleen, N.; 7426 Lake Neuchatel, Corpus Christi, TX 78413 (US). VICARI, Richard; 4618 Oso Parkway, Corpus Christi, TX 78413 (US). MURPHY, Carl, David; 446 Cole Street, Corpus Christi, TX 78404 (US).  <b>(74) Agents:</b> SPIERING, M., Susan; Hoechst Celanese Corporation, Patent Dept., P.O. Box 9077, Corpus Christi, TX 78469-9077 (US) et al.		08/516,853	18 August 1995 (18.08.95)	US	08/516,667	18 August 1995 (18.08.95)	US	08/516,587	18 August 1995 (18.08.95)	US	<b>(81) Designated States:</b> CN, JP, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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<b>(54) Title:</b> HYPERBRANCHED POLYMERS  <b>(57) Abstract</b>  The present invention provides novel highly branched macromolecule polymers that have highly controlled molecular architectures.											

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## HYPERBRANCHED POLYMERS

### BACKGROUND OF THE INVENTION

#### Field of the Invention

The present invention relates to novel highly branched macromolecule (hyperbranched) polymers that have highly controlled molecular architectures, and which have numerous applications such as chelating agents, rheology modifiers, and drug delivery vehicles.

#### Description of Related Art

The following prior art references are disclosed in accordance with the terms of 37 CFR 1.56, 1.97, and 1.98.

J. Chem. Soc. Perkin Trans. 1992 (p. 2459-2469) discloses a multi-step process for preparing highly branched macromolecules with aromatic polyester inner structure and a readily modified hydrophobic/hydrophilic surface.

Macromolecules 1993, 26, p. 4617-4623 discloses the synthesis of all-aromatic hyperbranched polyesters with phenol and acetate end groups. The synthesis was based on the melt condensation of the A<sub>2</sub>B monomers 3,5(bis-trimethylsiloxy)benzoyl chloride and 3,5-diacetoxybenzoic acid.

U.S. 5,041,516 discloses a multi-step convergent process for preparing polyesters from aliphatic and aromatic monomers.

U.S. 5,136,014 discloses polyesters prepared from aromatic and aliphatic monomers without a core group and which are capped.

U.S. 5,183,862 discloses capped polyesters prepared from aliphatic and aromatic monomers without a core group.

U.S. 5,196,502 discloses the use of diacetoxybenzoic acids and monoacetoxydibenzoic acids to produce wholly aromatic polyesters. This patent does not teach the use of a core monomer to increase the number of surface end groups in the polymer.

U.S. 5,225,522 discloses multiply-branched aliphatic-aromatic polyesters and processes for preparing the same; however, there is no disclosure of a core group.

U.S. 5,227,462 discloses multiply-branched aliphatic-aromatic polyesters and processes for preparing the same; however, there is no disclosure of a core group.

U.S. 5,266,106 discloses ink compositions with dendrimer grafts.

U.S. 5,306,561 discloses the preparation of surface-functional polymer particles.

U.S. 5,362,843 discloses a process for preparing highly branched macromolecule polymers.

5        U.S. 5,418,301 discloses a process for preparing dendritic macromolecules.

Other prior art publications which are of interest in this area include the following journal articles:

Turner, R.S.; Walter, F.; Voit, B.I.; Mourey, T.H. Macromolecules 1994, 27, 1611.

Turner, R.S.; Voit, B.I.; Mourey, T.H. Macromolecules 1993, 26, 4617.

10       Newkome, G.R.; Lin, X.; Weis, C.D. Tetrahedron: Asymmetry 1991, 2, 957.

Frechet, J.M.J. Science 1994, 263, 1710.

Frechet, J.M.J.; Hawker, C.J.; Wooley, K.L. Pure Appl. Chem. A31(11) 1994, 1627.

Wooley, K.L.; Frechet, J.M.J.; Hawker, C.J. Polymer 1994, 35, 4489.

Hawker, C.J.; Lee, R.; Frechet, J.M.J. J. Am. Chem. Soc. 1991, 113, 4583.

15       Jansen, J.F.G.A.; de Brabander Van der Berg, E.M.M.; Meijer, E.M. Science 1994, 266, 1226.

Kremers, J.A.; Meijer, E.W. J. Org. Chem. 1994, 59, 4262.

Seebach, D.; Lapierre, J.M.; Skobridis, K.; Greiveldinger, G. Angew. Chem. Int. Ed. Engl. 1994, 33, 440.

20       Seebach, D.; Lapierre, J.M.; Greiveldinger, G.; Skobridis, K. Helvetica Chimica Acta 1994, 77, 1673.

Kim, Y.H. J. Am. Chem. Soc. 1992, 114, 4947.

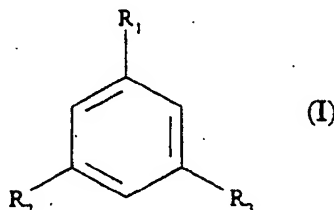
All of the above cited prior art and any other references mentioned herein are incorporated herein by reference in their entirety.

## 25        SUMMARY OF THE INVENTION

The present invention provides novel processes for preparing highly branched macromolecule polymers that have highly controlled molecular architectures. These types of polymers have utility in numerous areas such as engineering resins, fiber, film, bottle resins, rheology modifiers, drug delivery systems, membranes, chelating agents, catalyst support,

medical applications, analytical systems, and separation processes, in addition to being incorporated or copolymerized with other polymers such as polysulfone and polycarbonate.

The process comprises the reaction of a branching monomer ("monomer") such as a substituted phenyl compound having the formula:



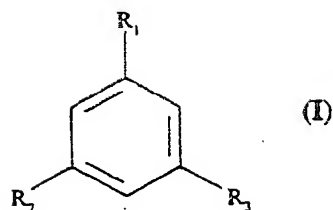
5 wherein  $R_1$ ,  $R_2$ , and  $R_3$  are defined below, with a novel second monomer ("an end-capping monomer"), hereinafter defined, such as a phenolic ester, for a sufficient period of time and at a sufficient temperature to produce the highly branched polymers in a single processing step.

#### DETAILED DESCRIPTION OF THE INVENTION

10 The present invention is directed to a novel process for preparing a highly branched polymer in a single step procedure. The present process utilizes the reaction of a certain class of substituted phenyl compounds (referred to herein as "branching monomer" or "monomer") with a new, novel class of polyfunctional molecules (herein referred to as "end-capping monomer") at a sufficient temperature and for a sufficient period of time to produce the highly branched polymer and which polymer is characterized by its high degree of branching, a  
15 branch point at each monomer unit, and a large number of chain ends or "surface" functional groups, resulting in a unique controlled macromolecular architecture. The end-capping monomer is further characterized as a monomer which contains functional groups which will only react with two of the three functional groups of the branching monomer. The desired end results are only achievable by using the herein described "new end-capping monomer" in each  
20 and every case in the condensation reaction. The use of the end-capping monomer is thus a critical feature, without which the maximum branching could not occur.

The branching monomer (hereinafter referred to as "monomer") is a substituted phenyl compound of the formula:

4



wherein  $R_1$  is from the group:

COOR where R is H, alkyl ( $C_1 - C_{20}$ ) or aromatic;

$C(O)-OC_6H_5$ ;

$O-CH_2CH_2OH$ ;

$O-C(O)-CH_3$ ;

$-N-CH_2CH_2OH$ ; and

$R_2$  is from the group:

COOR where R is H, alkyl ( $C_1 - C_{20}$ ) or aromatic;

OH;

$NH_2$ ;

$O-C(O)-CH_3$ ; and

$R_3$  is from the group:

COOR where R is H, alkyl ( $C_1 - C_{20}$ ) or aromatic;

OH;

$NH_2$ ; and

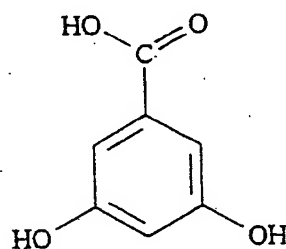
$O-C(O)-CH_3$ ;

- with the proviso that (a) when  $R_1$  is  $-COOH$ ,  $R_2$  and  $R_3$  must be the same but not equal to  $R_1$ , and  $R_2$  and  $R_3$  are either OH or  $O-C(O)-CH_3$ ; (b) when  $R_1$  is  $-C(O)-OC_6H_5$ ,  $R_2$  and  $R_3$  are equal and are either OH or  $NH_2$ ; and (c) when  $R_1$  is  $O-CH_2CH_2OH$ , or  $N-CH_2CH_2OH$ ,  $R_2$  and  $R_3$  are equal and  $R_2$  and  $R_3$  are  $-COOH$  (or  $-COOR_4$  wherein  $R_4$  is alkyl  $C_1-C_4$ ).

Typical branching monomers falling within the above monomer formula include:

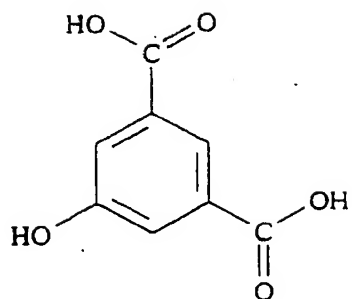
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1.



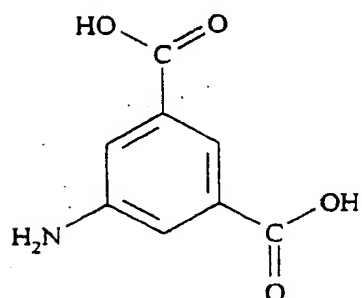
(II)

2.



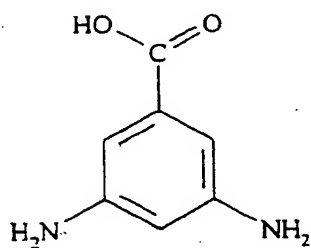
(III)

3.



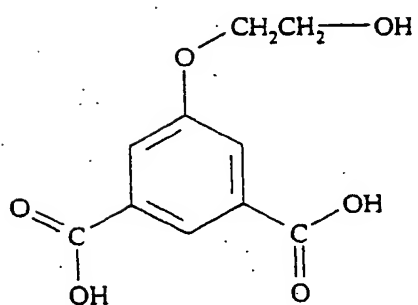
(IV)

4.



(V)

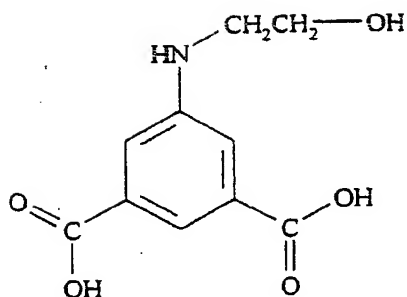
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(VI)

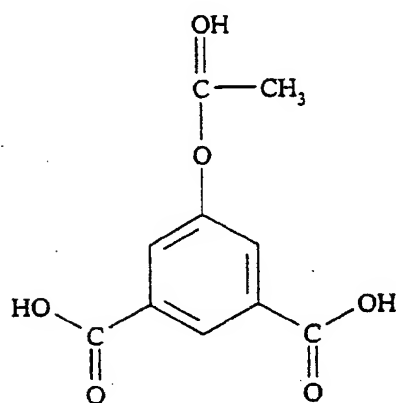
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6.



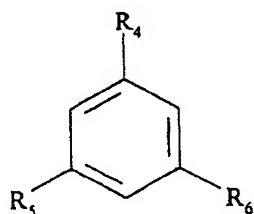
(VII)

7.



(VIII)

The end-capping monomer used in the present invention has the formula:

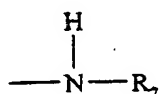


(IX)

wherein  $R_4$  is selected from the group consisting of COOR wherein R is H, alkyl

- 5 (C<sub>1</sub> to C<sub>20</sub>) or aromatic; C(O)-OC<sub>6</sub>H<sub>5</sub>; O-CH<sub>2</sub>CH<sub>2</sub>OH; O-C(O)-CH<sub>3</sub>; and N-CH<sub>2</sub>CH<sub>2</sub>OH.  $R_5$ , and  $R_6$  are each independently selected from the group consisting of:

(A)

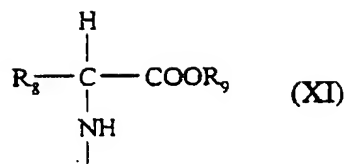


(X)

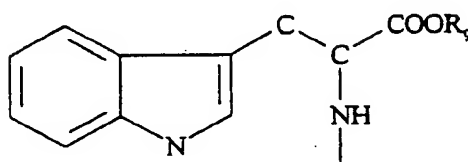
where  $R_7$  is a substituted or unsubstituted aryl or alkyl group;



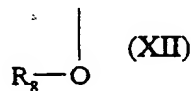
(B)



where  $\text{R}_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group and  $\text{R}_9$  is H or alkyl; e.g.

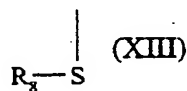


(C)



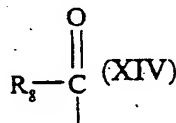
5 where  $\text{R}_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

(D)



where  $\text{R}_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

(E)



where  $\text{R}_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group; and

10 (F) chiral or racemic phosphine ligands.

In (E), Formula (XIV) above, this includes, without limitation, substituted or unsubstituted carboxylic acid or an optically active carboxylic acid selected from the group consisting of S-ibuprofen, S-naproxen, S-suprofen, S-flurbiprofen, S-indoprofen, S-keto-

profen, S-traprofenic acid, S-fenoprofen, S-butibufen, phenethicillin, S-2-chloropropionic acid, and ketorolac. Additional carboxylic acids are disclosed in U.S. 5,302,751 (Formula I), and which is incorporated herein by reference in its entirety. In (E), the C(O)- is -C(O)-OH in the above acids.

5           The phosphine ligands (both racemic and chiral) are those which are capable of attaching to carbon in formula (IX) above. Typical phosphine ligands that can be used herein are follows: bis(triphenylphosphine) dichloro complex, bis(tricyclohexylphosphine) dichloro complex, di-allyltriphenylphosphine dichloro complex, triphenylphosphine piperidine dichloro complex, bis(triphenylphosphine) (dicarbonyl complex, bis(triphenylphosphine)-diacetate  
10 complex, bis(triphenylphosphine) dinitrate complex, bis(triphenylphosphine) sulfate complex, tetrakis(triphenylphosphine) complex, and complexes in which some of the ligands are carbon monoxide such as chlorocarbonyl bis(triphenylphosphine) complex, all complexes with the end-capping monomer.

          Additional phosphine ligands are disclosed in U.S. 4,483,802; U.S. 5,041,228; U.S.  
15 5,057,618; German Patent DE 4,415,682, and Handbook of Enantioselective Catalysis, H. Brunner and W. Zettlmeier, Vols. I and II, VCH Verlagsgesellschaft mbH; and D-69451 Weinheim (Federal Republic of Germany) 1993, all of which are incorporated herein by reference in their entirety.

          In addition to the definitions of  $R_1$ - $R_8$  above,  $R_1$ - $R_8$  may also include alkyl, phenyl,  
20 naphthyl, substituted phenyl, substituted naphthyl, alkenyl, alkynyl, cycloalkyl, heteroaryl, substituted heteroaryl, alkoxyalkyl, and alkylthioalkyl.

          In the above definitions and throughout the present specification, alkyl means straight or branched chain alkyl having 1 to 20 carbon atoms, and includes, for example, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, secondary butyl, tertiary butyl, pentyl, isopentyl,  
25 neopentyl, hexyl, heptyl, octyl, 2-ethylhexyl, 1,1,3,3-tetramethylbutyl, nonyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, and eicosyl.

          Cycloalkyl means cyclic alkyl having 3 to 7 carbon atoms, and includes cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl.

          Alkenyl means straight or branched chain alkenyl having 2 to 8 carbon atoms, and  
30 includes, for example, vinyl, 1-propenyl, allyl, isopropenyl, 2-butenyl, 1,2-butanedieryl, 2-pentenyl, 2-hexenyl, and octenyl.

Alkynyl means straight or branched chain alkynyl having 2 to 8 carbon atoms, and includes, for example, ethynyl, 2-propynyl, butynyl, pentynyl, hexynyl, heptynyl, and octynyl.

Substituted phenyl and substituted naphthyl means phenyl or naphthyl substituted by at least one substituent selected from the group consisting of halogen (chlorine, bromine, fluorine, or iodine), amino, nitro, hydroxy, alkyl, alkoxy which means straight or branched chain alkoxy having 1 to 10 carbon atoms, and includes, for example, methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, secondary butoxy, tertiary butoxy, pentyloxy, isopentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, and decyloxy, haloalkyl which means straight or branched chain alkyl having 1 to 8 carbon atoms which is substituted by at least one halogen, and includes, for example, chloromethyl, bromomethyl, fluoromethyl, iodomethyl, 2-chloroethyl, 2-bromoethyl, 2-fluoroethyl, 3-chloropropyl, 3-bromopropyl, 3-fluoropropyl, 4-chlorobutyl, 4-fluorobutyl, dichloromethyl, dibromomethyl, difluoromethyl, diiodomethyl, 2,2-dichloroethyl, 2,2-dibromomethyl, 2,2-difluoroethyl, 3,3-dichloropropyl, 3,3-difluoropropyl, 4,4-dichlorobutyl, 4,4-difluorobutyl, trichloromethyl, 4,4-difluorobutyl, trichloromethyl, trifluoromethyl, 2,2,2-trifluoroethyl, 2,3,3-tri-fluoropropyl, 1,1,2,2-tetrafluoroethyl, and 2,2,3,3-tetrafluoropropyl.

Heteroaryl means 5 to 10 membered mono- or fused-heteroaromatic ring which has at least one heteroatom selected from the group consisting of nitrogen, oxygen, and sulfur, and includes, for example, 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, pyrazolyl, imidazolyl, pyrimidinyl, pyridazinyl, pyrazinyl, benzimidazolyl, quinolyl, oxazolyl, thiazolyl, and indolyl.

Substituted heteroaryl means 5 to 10 membered mono- or fused-heteroaromatic ring which has at least one heteroatom selected from the group consisting of nitrogen, oxygen, and sulfur and which is substituted by at least one substituent selected from the group consisting of halogen, amino, nitro, hydroxy, alkyl, alkoxy, and haloalkyl on the above-mentioned heteroaromatic nucleus.

Haloalkyl means straight or branched chain alkyl having 1 to 10 carbon atoms which is substituted with at least one halogen as mentioned above.

Alkoxyalkyl means that the alkoxy moiety and the alkyl moiety each are straight or branched chain ones having 1 to 8 carbon atoms, and includes, for example, methoxy-methyl, ethoxymethyl, propoxymethyl, isopropoxymethyl, butoxymethyl, isobutoxymethyl, tertiary

butoxymethyl, penryloxymethyl, hexyloxymethyl, heptyloxymethyl, octyloxy- methyl, 2-methoxyethyl, 2-ethyloxyethyl, 2-propoxyethyl, 2-butoxyethyl, 2-hexyloxyethyl, 2-octyloxyethyl, 3-methoxypropyl, 3-ethoxypropyl, 3-propoxypropyl, 3-butoxypropyl, 3-hexyloxypropyl, 3-octyloxypropyl, 4-methoxybutyl, 4-ethoxybutyl, 4-propoxybutyl, 4-butoxybutyl, 4-hexyloxybutyl, 4-octyloxybutyl, 5-methoxypentyl, 5-ethoxypentyl, 5-propoxypentyl, 5-butoxypentyl, 5-pentyloxyphenyl, 5-hexyloxypentyl, 5-octyloxypentyl, 6-methoxyhexyl, 6-ethoxyhexyl, 6-propoxyhexyl, 6-butoxyhexyl, 6-pentyloxyhexyl, 6-hexyloxyhexyl, 6-octyloxyhexyl, 8-methoxyoctyl, 8-ethoxyoctyl, 8-butoxyoctyl, 8-hexyloxyoctyl, and 8-octyloxyoctyl.

Alkylthioalkyl means that the alkylthio moiety and the alkyl moiety each are straight or branched chain ones having 1 to 8 carbon atoms, and includes, for example, methylthiomethyl, ethylthiomethyl, propylthiomethyl, isopropylthiomethyl, butylthiomethyl, isobutylthiomethyl, tertiary butylthiomethyl, pentylthiomethyl, hexylthiomethyl, octylthiomethyl, 2-methylthioethyl, 2-ethylthioethyl, 2-butylthioethyl, 2-hexylthioethyl, 3-methylthiopropyl, 3-ethylthiopropyl, 3-propylthiopropyl, 3-butylthiopropyl, 4-methylthiobutyl, 4-ethylthiobutyl, 4-propylthiobutyl, 4-butylthiobutyl, 6-methylthiohexyl, 6-ethylthiohexyl, 6-butylthiohexyl, 8-methylthiooctyl, 8-ethylthiooctyl, and 8-butylthiooctyl.

Phenylalkyl means that the alkyl moiety is straight or branched chain alkyl having 1 to 8 carbon atoms and includes, for example, benzyl, 2-phenylethyl, 1-phenylethyl, 3-phenylpropyl, 4-phenylbutyl, 5-phenylpentyl, 6-phenylhexyl, and 8-phenyloctyl.

Substituted phenylalkyl means above-mentioned phenalkyl which is substituted by at least one substituent selected from the group consisting of halogen, amino, nitro, hydroxy, alkyl, alkoxy, and haloalkyl on the phenyl nucleus.

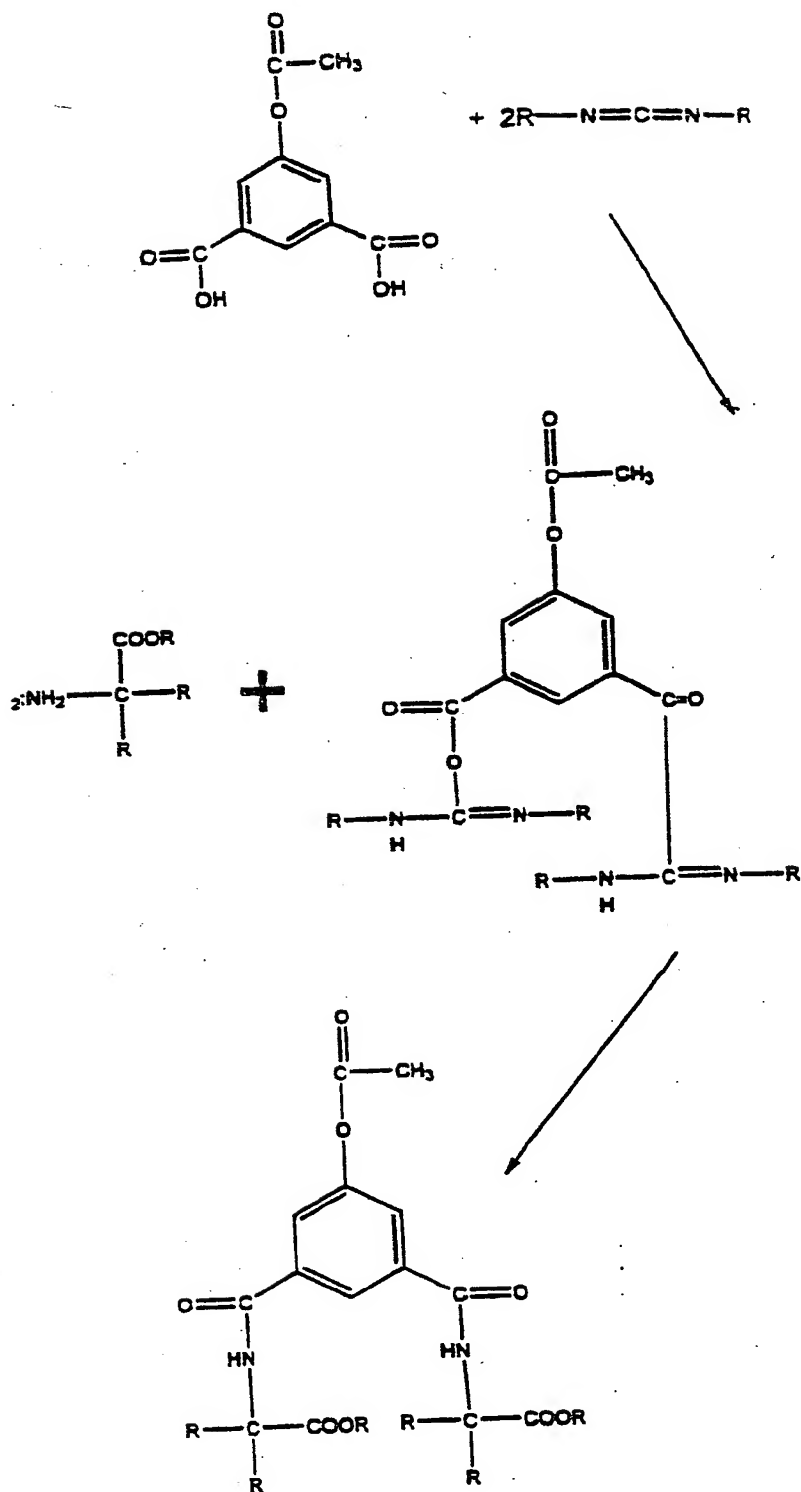
Heteroarylalkyl means that the heteroaryl moiety is 5 to 10 membered mono- or fused-heteroaromatic ring having at least one heteroatom selected from the group consisting of nitrogen, oxygen, and sulfur as mentioned above and the alkyl moiety is straight or branched chain alkyl having 1 to 8 carbon atoms and includes, for example, furfuryl, 3-furylmethyl, 2-thienyl, 3-thienyl, 2-, 3-, or 4-pyridylmethyl, pyrazoylmethyl, 1-imidazolylmethyl, pyrimidinylmethyl, benzimidazolylmethyl, 2-(2-furyl)ethyl, 2-(2-thienyl)-ethyl, 2-(2-pyridyl)ethyl, 2-(1-imidazolyl)ethyl, 3-(2-furyl)propyl, 3-(2-thienyl)-propyl, 3-(2-pyridyl)propyl, 3-(2-pyridyl)propyl, 4-(2-furyl)butyl, 4-(2-thienyl)butyl, and 4-(2-pyridyl)butyl.

Substituted heteroarylalkyl means that the substituted heteroaryl moiety is 5 to 10 membered mono- or fused-heteroaromatic ring which is substituted by at least one substituent selected from the group consisting of halogen, amino, nitro, hydroxy, alkyl, alkoxy, and haloalkyl on the heteroaryl nucleus and which has at least one heteroatom selected from the group consisting of nitrogen, oxygen, and sulfur as mentioned above, and that the alkyl moiety is straight or branched chain alkyl having 1 to 8 carbon atoms.

Cycloalkylalkyl means that the cycloalkyl moiety is cyclic alkyl having 3 to 7 carbon atoms and the alkyl moiety is straight or branched chain alkyl having 1 to 8 carbon atoms, and includes, for example, cyclopropylmethyl, cyclobutylmethyl, cyclopentyl- methyl, cyclohexylmethyl, cycloheptylmethyl, 2-cyclopropylethyl, 2-cyclopentylethyl, 2-cyclohexylethyl, 3-cyclopropylpropyl, 3-cyclopentylpropyl, 3-cyclohexylpropyl, 4-cyclopropylbutyl, 4-cyclopentylbutyl, 4-cyclohexylbutyl, 6-cyclopropylhexyl, and 6-cyclohexylhexyl.

The end-capping monomer (i.e. the substituted aryl group) is prepared, in general, by reacting an aromatic acid with, for example, an activating carbodiimide (see Tetrahedron: Asymmetry 1991 above for examples of such activating carbodiimide) to form an activated intermediate which is then reacted with a nucleophile to form said substituted aryl group. These reactions are carried out at temperatures in the range of from about -20°C to about 120°C, preferably from about 0°C to about 35°C. The pressure is not critical and thus can be subatmospheric, atmospheric, or super atmospheric. A typical process of preparing an end-capping monomer is shown in Scheme 1.

12

SCHEME 1

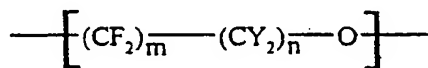
Furthermore, and as used herein, the term "substituted" is contemplated to include all permissible substituents of organic compounds. In a broad aspect, the permissible substituents include acyclic and cyclic, branched and unbranched, carbocyclic and heterocyclic, aromatic and non-aromatic substituents of organic compounds. Illustrative substituents include, for example, those described hereinabove. The permissible substituents can be one or more and the same or different for appropriate organic compounds. For purposes of this invention, the heteroatoms such as nitrogen may have hydrogen substituents and/or any permissible substituents of organic compounds described herein which satisfy the valencies of the heteroatoms. This invention is not intended to be limited in any manner by the permissible substituents of organic compounds.

The reaction of the branching monomer with the end-capping monomer may be carried out in the presence of an inert diluent which has a boiling point of from about 200°C to about 350°C, preferably from about 220°C to about 300°C.

Suitable diluents which assist in achieving the objects of the present invention include, without limitation, diphenyl ether, halogenated diphenyl ether, diphenyl sulfone, benzophenone, polyphenyl ethers such as tri and tetraphenyl ether, terphenyl, tetraphenyl, halogenated biphenyl, and the like.

These and other suitable diluents are disclosed in U.S. Patent 3,948,856 and Ing. Eng. Chem. Prod. Res. Dev., Vol. 20, No. 2, 1981; both of these are incorporated herein by reference in their entirety.

Other suitable diluents include a poly (fluorinated alkylene oxide) having repeating units as follows:



wherein m is an integer from 1 to 10, n is an integer from 0 to 5, Y is the same or different and represents hydrogen or halogen including F, Cl or Br. The poly(fluorinated alkylene oxide) can be either a straight or branched chain structure.

It is preferred that the polyether diluent be perfluorinated. Examples of the useful aliphatic polyethers used in the present invention include poly(tetrafluoroethylene oxide), poly(hexafluoropropylene oxide), poly(fluorinated butylene oxide), copolymers formed from different fluorinated alkylene oxides; etc. The polyethers used in the present invention are a non-solvent for the highly branched polymer which is formed and further, will separate from

the acetic acid by-product to form a separate layer therefrom. Thus, removal of the diluent can be achieved by decantation of the diluent layer which then can be recycled to the polymerization stage. The polyether diluents used in this invention are non-flammable and non-toxic.

5       The poly(fluorinated alkylene oxides) used in the present invention are of relatively low molecular weight. Thus, molecular weights ( $M_n$ ) of about 600 to 20,000 are typical with molecular weights of about 600 to 5,000 being more typical and preferred.

10       The diluent used, if desired, in the present invention should be present in amounts of from about 10 to about 60 wt. % based on the weight of the total charge. Preferred amounts of the diluent range from about 10 to about 40 wt. % and most preferably from about 10 to 30 wt. % based on total charge.

      The amount of the diluent can vary during the polymerization reaction. For example, it may be advantageous to increase progressively the amount of the diluent to maintain the reaction medium at about constant viscosity.

15       It is also within the scope of the present invention to employ a reaction catalyst or a mixture of reaction catalysts. The overall objective is to use catalysts to accelerate the rate of polymerization of the reaction mixture. These catalysts are sometimes called esterification catalysts.

20       All the conventional catalysts being capable of accelerating an ester exchange reaction are usable. Suitable examples of catalysts are salts or compounds of elements selected from Groups 1A, 2A, 2B, 3A, 4A, and 5A of the periodic table of elements. Examples include metal oxides (e.g., magnesium oxide, lead oxide, zinc oxide, antimony trioxide); alkoxides which are prepared by the reaction of an alcohol or glycol and an alkali metal, alkaline earth metal, aluminum or titanium; sodium acetate and sodium benzoate; metal hydrides and metal  
25       borohydrides (e.g., lithium hydride, potassium borohydride ( $K_2B_2H_6$ )). One preferred catalyst is an alkali metal salt and most preferred are lithium and potassium salts including the acetates, carbonates, benzoates, formates, bicarbonates, hydroxides, phosphates, and monohydrogen phosphates of lithium or potassium. The lithium salts are especially preferred including lithium acetate, carbonate, and hydroxide. The catalyst is added in amounts between about 5  
30       to 100 ppm based on end-capping monomer, preferably about 20 to 50 ppm, and most preferably about 25 ppm.



Additional catalysts may also be used, in combination with the above described catalysts. Examples include the imidazole catalysts disclosed in U.S. Patent 4,612,360 incorporated herein by reference in its entirety. Specific examples include 1-methylimidazole, 1-ethylimidazole, 2-ethyl-4-methylimidazole, and benzimidazole.

5 A cobalt salt may be added to the reaction medium along with the catalyst, to act as co-catalyst and as well to yield a highly branched polymer of suitable color, in particular, improved Hunter b color in which the yellowness of the highly branched polymer is substantially reduced. Cobalt has a catalytic effect in the overall process and can reduce the yellow color in the "as-prepared" highly branched polymer formed by the present process.

10 Any cobalt salt may be used as the co-catalyst to improve highly branched polymer color, including but not limited to, cobalt acetate, cobalt benzoate, cobalt carbonate, cobalt phenate, and the cobalt salt of aliphatic or isoaliphatic carboxylic acids which contain 3 to 20 carbon atoms, such as cobalt 2-ethylhexanoate. The cobalt salt can be added directly to the monomeric components or, more preferably, to insure solubility and uniform dispersion of the  
15 cobalt salt, the cobalt salt can be dissolved in the said diluent prior to addition. In general, the cobalt salt can be added in sufficient amounts to yield at least about 20 ppm, preferably at least 25 ppm of cobalt in the final highly branched polymer. Below these levels, some color improvement has been found although water white color is not achieved. More preferably, the amount of cobalt should range from about 30 ppm to 60 ppm based on the final polymer. The  
20 preferred highly branched polymer color has a value of less than 2.0 on the Hunter b scale.

The process of this invention is carried out at a polymerization temperature of at least 25°C, preferably from about 25°C to about 275°C, and more preferably, from about 150°C to about 250°C. The present process, where one so desires, may be conducted in an inert atmosphere (such as argon or nitrogen). It is desirable to maintain the reaction temperature as  
25 low as possible to prevent the coloration of polymer while as high a reaction temperature as possible is preferred in terms of the rate of reaction. The process is initially carried out at atmospheric pressure or super atmospheric pressure and the pressure can be reduced as polymerization proceeds. Near the end of polymerization, pressure as low as 0.1 mm Hg absolute may be used.

30 The polymerization reaction is conducted for a period of time sufficient to produce a highly branched polymer and which time is generally in the range of from about 1/2 hour to about 8 hours or longer, depending on the particular highly branched polymer being prepared.

The polymerization reaction of this invention may be carried out batchwise or continuously by using appropriate staging and by using suitable apparatus. Moreover, the reactants may be added to the polymerization zone in any way or order desired.

5 The ester derivatives of the end-capping monomer and the branching monomer may be formed in situ by adding the monomer together with the acid anhydride, said diluent, and the reaction catalyst to the reactor and the reaction carried out in a single reaction zone under combined esterification and polymerization conditions as described above. Additionally, the ester derivative of the end-capping monomer and the branching monomer may be first prepared and then a diluent and reaction catalyst added directly to the same reaction vessel  
10 with the polymerization being carried out under the conditions described above.

The highly branched polymer having the desired characteristics is recovered in its final form by methods well known to those in the art, such as by direct devolatilization in an extruder under conditions sufficient to remove the by-product compound, coagulation, spray drying, and the like.

15 The highly branched polymers may be prepared in the presence of materials such as molecular weight regulators, antioxidants, and the like. The highly branched polymers obtained by the process of this invention may be used together with the well-known additives such as plasticizers, pigments, lubricating agents, mold release agents, stabilizers, inorganic fillers, and the like. These highly branched polymers may also be blended with other  
20 polymers.

The following specific examples are supplied for the purpose of better illustrating the invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters, or values which must be utilized exclusively in order to practice the present invention.

25

### EXAMPLE 1

#### Preparation of 5-Acetoxyisophthalic Acid from 5-Hydroxyisophthalic Acid (Branching Monomer)

5-Hydroxyisophthalic acid (360.56 g, 1.98 moles) was charged to a 2000 mL round bottom 3-neck flask with a Friedrich condenser and thermocouple under a blanket of nitrogen.  
30 Acetic anhydride (808.25 g, 7.96 moles) was added slowly. The white suspension was stirred and refluxed (-136°C) for 4 hours. After cooling the white solid was filtered off and washed

with toluene. Yield of 5-acetoxyisophthalic acid (336.95 g, 76%, HPLC 97% purity). DSC m.p. 208°C. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ 13.33, 8.34, 7.88, 2.31. <sup>13</sup>C NMR (100 MHz, d<sub>6</sub> DMSO) δ 169.07, 165.76, 150.63, 132.69, 127.11, 126.57, 20.79.

### EXAMPLE 2

#### 5 Preparation of 3,5-Diacetoxybenzoic Acid from 3,5-Dihydroxybenzoic Acid (Branching Monomer)

3,5-Dihydroxybenzoic acid (446.42 g, 2.89 moles) was charged to a 2000 mL round bottom 3-neck flask with a Friedrich condenser and thermocouple under a blanket of nitrogen. Acetic anhydride (1515 g, 14.85 moles) was added slowly. The suspension was stirred and  
10 refluxed (~135°C) for 3 hours. After cooling, the cream solid was filtered off and washed with toluene. The acetic anhydride was removed under reduced pressure 2 more times to yield additional cream solids. Yield of 3,5-diacetoxybenzoic acid (347.02 g, 50%, HPLC 97.5% purity). DSC m.p. 155°C. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ 13.31, 7.59, 7.28, 2.29. <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO) δ 169.20, 166.01, 151.15, 133.12, 120.53, 120.32, 20.70 MS  
15 (DIP) m/e 238 (M<sup>+</sup>).

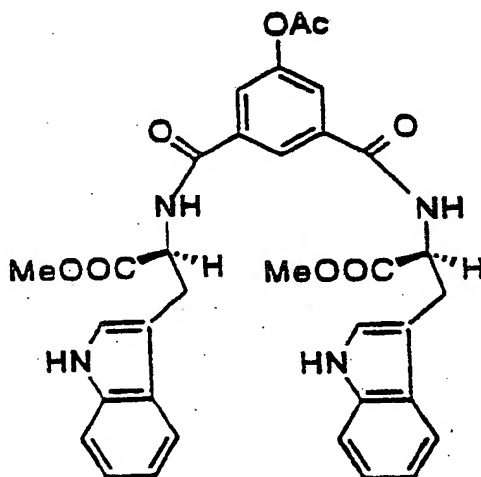
### EXAMPLE 3

#### Preparation of 2-{3-Acetoxy-5-[2-(1H-Indol-2-yl)-1-Methoxycarbonyl-Ethylcarbamoyl]-Benzoylamino}-3-(1H-Indol-2-yl)-Propionic Acid Methyl Ester (End Capping Monomer)

Acetoxyisophthalic acid (13.44 g, 0.06 moles) dissolved in tetrahydrofuran (ca. 250  
20 mL) and 1,3-dicyclohexylcarbodiimide (27.26 g, 0.132 moles) dissolved in acetonitrile (ca. 270 mL) were added to a suspension of L-tryptophan methyl ester hydrochloride (33.69 g, 0.132 moles) in acetonitrile (ca. 1L) under nitrogen. Triethylamine (13.72 g, 0.132 moles) was added dropwise to the suspension. After stirring at ambient temperature for 2 days, the yellow solution with white precipitate was filtered and the solvent removed under reduced  
25 pressure. The residue was taken up in methylene chloride (ca. 400 mL) and filtered. The organic layer was extracted with water (1 x 300 mL), 5% acetic acid (3 x 300 mL), water (3 x 300 mL), dried (MgSO<sub>4</sub>), filtered, and the solvent removed under reduced pressure to yield a cream foam (40.72 g, yield > 100%, purity by HPLC 64%). Chromatography of the solid on silica gel with THF/methylene chloride (1:5) gave a material yield of 68%, HPLC average  
30 purity 84%. [α]<sub>D</sub> = -57.105° (c = 1.14, methanol) HPLC purity 96%. DSC ~115°C

(broad).  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  10.84(d, 2H, HN(trp)), 9.06 (d, 2H, NH), 8.28 (s, 1H, Ar-H), 7.79 (s, 2H, Ar-H), 7.59 (d, 2H, Ar-H(trp)), 7.35 (d, 2H, Ar-H(trp)), 4.79 (m, 2H, C\*), 3.66 (s, 6H,  $\text{COOCH}_3$ ), 3.31 (m, 4H,  $\text{CH}_2$ ), 2.35 (s, 3H,  $\text{COCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  172.27 ( $\text{COOCH}_3$ ), 169.09 ( $\text{COCH}_3$ ), 164.93 (CON), 150.17 (Ar-C), 136.12 (indolyl-C), 135.28 (Ar-C), 127.05 (indolyl-C), 124.27, 123.81, (Ar-C), 123.56, 120.98, 118.42, 117.98, 111.45, 109.86 (indolyl-C), 53.98 (C\*H-NH), 51.91 ( $\text{COOCH}_3$ ), 26.61 ( $\text{CH}_2$ ), 20.69 ( $\text{COCH}_3$ ), 26.61 ( $\text{CH}_2$ ), 20.69 ( $\text{COCH}_3$ ). FTIR (KBr)  $\nu$  3393 (b, NH indole, NH amide), 1766 (sh, C=O), 1731 (s, C=O), 1647 (s, CO amide)  $\text{cm}^{-1}$ . MS(APCI( $\text{H}_2\text{O}$ ) + Q1)  $m/e$  625.4 (M+1).

This end-capping monomer has the following structure:



(XV)

#### EXAMPLE 4

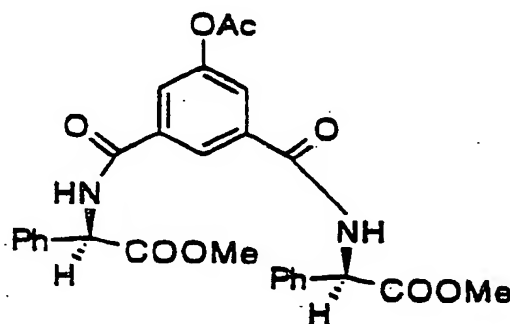
##### Preparation of [3-Acetoxy-5-(Methoxycarbonyl-Phenyl-Methylcarbamoyl)-Benzoylamino]-Phenyl-Acetic Acid Methyl Ester (End Capping Monomer)

Acetoxyisophthalic acid (5.38 g, 0.024 moles) dissolved in tetrahydrofuran (ca. 75 mL) and 1,3-dicyclohexylcarbodiimide (10.48 g, 0.05 moles) dissolved in tetrahydrofuran (ca. 50 mL) were added to a suspension of (R)-(-)-2-phenylglycine methyl ester hydrochloride (10.45 g, 0.05 moles) in acetonitrile (45 mL) under nitrogen. Triethylamine (5.33 g, 0.05 mL) was

added dropwise over 5 minutes to the suspension. After stirring at ambient temperature for 5 days, the yellow solution with a white precipitate was filtered and the solvent was removed under reduced pressure. The residue was taken up in methylene chloride (ca. 500 mL) and filtered. The organic layer was extracted with water (1 x 300 mL), 5% acetic acid (3 x 120 ml), water (3 x 150 mL), dried (MgSO<sub>4</sub>), filtered, and the solvent removed under reduced pressure to yield a cream solid (12.76 g, yield > 99%, purity by HPLC 63%).

Chromatography of the solid on silica gel with ethyl acetate/hexane (5:2) gave a material yield of 62%, HPLC average purity 77%. Analytical sample (HPLC 95%).  $[\alpha]^{20} = -136.02^\circ$  (c=0.98, THF). DSC m.p. 214-219°C. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO)  $\delta$  9.38 (d, 2H, NH), 8.33 (1H, Ar-H), 7.85 (2H, Ar-H), 7.48 (m, 4H, Ar-H), 7.37 (m, 6H, Ar-H), 5.67 (d, 2H, HNCH), 3.66 (s, 6H, OMe), 2.30 (s, 3H, Me). <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO)  $\delta$  170.82 (COOMe), 169.07 (COMe), 165.1 (CONH), 150.08, 135.84, 134.93, 128.52, 128.25, 124.78, 124.24, (Ar-C), 57.05 (HNCH), 52.24 (OMe), 20.66 (Me). FTIR (KBr)  $\nu$  3330, 3281, 3027, 2943, 1759 (sh), 1731 (s, C=O), 1639 (s, C=O) cm<sup>-1</sup>. MS(APCI(H<sub>2</sub>O) + Q1) m/e 519.2 (M+1).

This end-capping monomer has the following structure:



(XVI)

### EXAMPLE 5

#### Preparation of Poly-(5-Hydroxyisophthalic Acid), (R)-2-Phenylglycine Methyl Ester Terminated Hyperbranched Polymer

The end-cap (Example 4), [3-acetoxy-5-(methoxycarbonyl-phenyl-methyl-carbamoyl)-benzoylamino]-phenyl-acetic acid methyl ester (6.29 g, 0.012 moles) was weighed into a 250 mL round bottom 1-neck flask. 5-Acetoxyisophthalic acid (3.03 g, 0.011 moles) was added to the flask. The flask was attached to an RE 111 Rotary Evaporator with a nitrogen blanket

over the solids. The flask was rotated in an oil bath at a slow speed, approximately 1 rotation per second with heating. The mixture melted to a clear orange liquid in approximately 15 minutes at 206°C. After 30 minutes of heating, vacuum (~2.5 mmHg) was applied for 20 minutes and acetic acid distilled off. The dark red solid was cooled with rotation under vacuum to 70°C and to ambient temperature under nitrogen. The solid was refluxed with tetrahydrofuran (170 mL) and water (17 mL) under nitrogen until dissolved (~10 minutes). The cooled solution was filtered and the solvent removed under reduced pressure. The residue was taken up in THF and filtered. The THF solution was added to water (700 mL) with stirring to precipitate the hyperbranched polymer. The hyperbranched polymer was filtered and dried to give an orange solid (2.62 g).  $[\alpha]^{20} = -2.979^\circ$  (c=0.94, THF). GPC [THF using 4 Waters Ultrastaygel 7.8 mm x 300 mm with 7 micron particle columns; standard polystyrene molecular weights 1800 to 500,000] Mw = 1373 Daltons, polydispersity 1.6. TGA, -257°C, <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ 13.3 (vs), 9.41 (m), 8.42-7.85 (m), 7.47 (b), 7.34 (b), 5.68 (m), 3.66, 2.32 (m), THF peaks present. <sup>13</sup>C NMR (50 MHz, d<sub>6</sub>-DMSO) δ 171.31, 166.82 - 163.57 (m), 158.24 (b), 150.90, 136.36 (m), 130.59 (m), 119.79 (m), 56.96 (m), 52.23 (m), 20.74 (m), THF peaks present.

#### EXAMPLE 6

##### Preparation of Poly-(5-Hydroxyisophthalic Acid). (S)-Tryptophan Methyl Ester Terminated Hyperbranched Polymer

The end-cap (Example 3) compound (10.2 g, 0.016 moles) was weighed into a 500 mL round bottom 1-necked flask. 5-Acetoxyisophthalic acid (7.18 g, 0.032 moles) was added to the flask. The flask was attached to a RE111 Rotary Evaporator with a nitrogen blanket over the solids. The flask was rotated in an oil bath at a slow speed, approximately 1 rotation per second with heating. The mixture melted to a yellow liquid at 215°C. After 15 minutes of heating, vacuum (~4mmHg) was applied for 30 minutes. The red solid was cooled with rotation under vacuum. The solid was refluxed with tetrahydrofuran (~100mL) under nitrogen for 1 hour. The cooled solution was filtered, reduced to a smaller volume of THF and 2-propanol was added to precipitate the hyperbranched polymer. The hyper-branched polymer was filtered and dried to give a yellow solid (2.11g, 15%).  $[\alpha]^{20} = -39.4^\circ$  (c=1.444, DMF). GPC Mw=5228 Daltons, polydispersity 1.4. TGA, -262°C. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ 10.80, 9.06 (b), 8.8-6.9 (m), 4.73 (b), 3.62 (b), 3.26(vb) 2-propanol peaks

present.  $^{13}\text{C}$  NMR (50 MHz,  $d_6$ -DMSO)  $\delta$  172.49, 166.02 (m), 154.10, 163.13 (m), 150.94 (b), 136.26, 135.59, 128.35 (m), 127.19, 124.90, 123.75, 121.11, 118.55 (m), 118.12, 111.59, 109.93, 54.02, 51.97 (m), 26.57, 2-propanol peaks present.

The THF/2-propanol filtrate was evaporated down and a second precipitation of yellow hyperbranched polymer (2.35g, 16%) was collected.  $[\alpha]^{20} = -42.805^\circ$  ( $c=1.0980$ , DMF). GPC  $M_w=3695$  Daltons, polydispersity 1.4.

The filtrate contained an orange-red solid (8.67 g, 60%). GPC  $M_w=1496$  Daltons, polydispersity 1.4.

### EXAMPLE 7

#### 10 Preparation of Poly-(3,5-Dihydroxybenzoic Acid). (S)-(+)-Ibuprofen Terminated Hyperbranched Polymer

(S)-(+)-Ibuprofen (10.01 g, 0.049 moles) was weighted into a 250 mL round bottom 1-necked flask. 3,5-Diacetoxybenzoic acid (12.06 g, 0.046 moles, Example 2) was added to the flask. The flask was attached to a RE111 Rotary Evaporator with a nitrogen blanket over the solids. The flask was rotated in an oil bath at a slow speed, approximately 1 rotation per second with heating. The mixture melted to a clear cream liquid in approximately 10 minutes at  $162^\circ\text{C}$ . After 40 minutes of heating at  $200^\circ\text{C}$ , vacuum ( $\sim 1.75$  mmHg) was applied for one hour and acetic acid distilled off. The cream solid was cooled under nitrogen to ambient temperature. The solid was refluxed 60 minutes with tetrahydrofuran (110 mL) under nitrogen. The cooled solution was filtered and half the solvent removed under reduced pressure. The THF solution was added to methanol (400 mL) with stirring to precipitate the hyperbranched polymer. The hyper- branched polymer was filtered and dried to give a cream solid (12.79 g,  $\sim 79\%$ ).  $[\alpha]^{20} = +6.298^\circ$  ( $c=2.08$ , THF). GPC  $M_w=21805$  Daltons, polydispersity 2.7. TGA,  $390^\circ\text{C}$ ,  $^1\text{H}$  NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  8.03 (b), 7.83-7.51 (m), 7.27 (b), 4.04 (b), 2.38 (b), 2.28 (b), 1.73, 1.49 (b), 0.833 (b), THF peaks presents.  $^{13}\text{C}$  NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  172.76, 168.73, 162.60, 151.01, 140.04, (m), 136.95, 130.61 (b), 127.13, 121.19 (m), 44.12, 29.42, 21.89, 20.63, 18.44 (m), THF peaks present.

### EXAMPLE 8

#### 30 Preparation of Poly-(3,5-Dihydroxybenzoic Acid). Benzoic Acid Terminated Hyperbranched Polymer

3,5-Diacetoxybenzoic acid (63.50 g, 0.303 moles) was weighted into a 500 mL round bottom 1-necked flask. Benzoic acid (40.47 g, 0.328 moles) was added to the flask. The flask was attached to a RE111 Rotary Evaporator with a nitrogen blanket over the solids. The flask was rotated in an oil bath at a slow speed, approximately 1 rotation per second with heating. The mixture melted to a yellow liquid in approximately 20 minutes at 190°C. After 47 minutes of heating at 200°C, vacuum (~1 mmHg) was applied for one hour and acetic acid distilled off. The cream solid was cooled under vacuum to ambient temperature. The solid was refluxed 60 minutes with tetrahydrofuran (400 mL) under nitrogen. THF (200 mL) was added to the cooled solution and the solution was filtered. Half the solvent was removed under reduced pressure. The THF solution was added to methanol (1000 mL) with stirring to precipitate the hyperbranched polymer. The hyperbranched polymer was filtered and dried to give a cream solid (50.29 g). GPC Mw=68015 Daltons, polydispersity 4.0. TGA -345°C. <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ 10.35 (b), 8.09 (b), 7.85 (b), 7.60 (b), 7.39 (b), 2.27 (b), methanol and water peaks present. <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO) δ 168.81, 162.69, 135.00, 130.65-128.88 (m), 121.82-120.83 (m), 20.67, THF and methanol peaks present.

### EXAMPLE 9

#### Preparation of Poly-(5-Hydroxyisophthalic Acid), (S)-Tryptophan Methyl Ester Terminated Hyperbranched Polymer

The end-cap (Example 3) compound (6.45 g, 0.0098 moles, HPLC purity 66.3%) was weighed into a 500 mL round bottom 1-necked flask. 5-Acetoxyisophthalic acid (3.68 g, 0.0091 moles) was added to the flask. The flask was attached to a RE111 Rotary Evaporator with a nitrogen blanket over the solids. The flask was rotated in an oil bath at a slow speed, approximately 1 rotation per second with heating. The mixture melted to a yellow-orange liquid at 221°C in 30 minutes. After 15 minutes of heating under nitrogen, vacuum (~1.5 mmHg) was applied for 30 minutes. The red solid was cooled with rotation under vacuum. The solid was refluxed with tetrahydrofuran (200 mL) under nitrogen for 10 minutes. The cooled solution was filtered, reduced to a smaller volume of THF and poured into water (700 mL) to precipitate the hyperbranched polymer. The hyperbranched polymer was filtered and dried to give an orange solid (6.62 g)  $[\alpha]^{20} = -4.06^\circ\text{C}$  (c=3.82, THF). GPC Mw=2103 Daltons, polydispersity 1.7. TGA, 259°C (onset). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO) δ 10.80, 9.05 (b), 8.63 - 6.97 (m), 4.76 (b), 3.63 (b), 2.33, THF peaks present. <sup>13</sup>C NMR (100



MHz,  $d_6$ -DMSO)  $\delta$  172.42, 169.08 (m), 166.09 - 163.08 (m), 151(m), 136.10 - 118.40 (m), 111.44, 109.94, 53.85 (m), 51.85 (m), 26.61, THF peaks present.

### EXAMPLE 10

#### Preparation of Poly-[2,2-Bis(Hydroxymethyl)Propionic Acid] Hyperbranched Polymer

5           2,2-Bis(hydroxymethyl)propionic acid (10.33 g, 0.077 moles) was weighed into a 500 mL round bottom 1-necked flask. The flask was attached to a RE111 Rotary Evaporator with a nitrogen/argon blanket over the solids. The flask was rotated in an oil bath at a slow speed, approximately 1 rotation per second with heating. The mixture melted to a clear liquid in approximately 25 minutes at 200°C. After 13 minutes of heating at 200°C, vacuum (~3.25  
10 mmHg) was applied for 1.3 hours and water distilled off. The clear pale yellow solid was cooled under vacuum to ambient temperature. Starting material was removed from the neck of the flask and THF (~100 mL) was added to the clear glassy solid. After standing over night the white starting material was removed and the THF removed under reduced pressure to give a clear semi-solid (5.6 g). GPC Mw = 1768 Daltons, polydispersity 1.6. TGA -270°C. 1H  
15 NMR (400 MHz,  $d_6$ -DMSO)  $\delta$  11.65, 4.9 (b), 4.59(b), 4.06, 3.47(m), 1.06(m). 13C NMR (100 MHz,  $d_6$ -DMSO)  $\delta$  174.3(m), 173.1(m), 63.88(bm), 50.25 - 45.64(m), 16.87 (m).

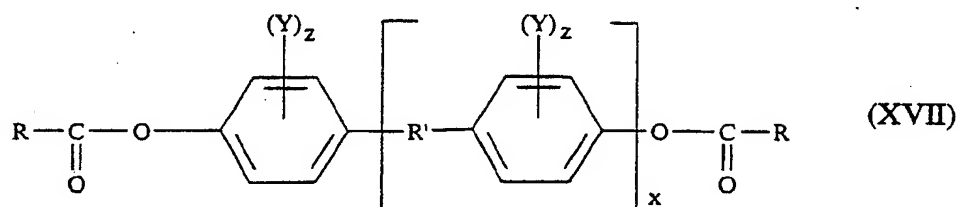
### EXAMPLE 11

In order to demonstrate the chelating utility of this highly branched polymer, 10 g of the polymer is produced according to the process described in Example 5. A 1% solution of  
20 copper sulfate (1000 ppm CuSO<sub>4</sub>) is combined with 100 ml of water to produce a light blue solution containing copper ions. The 10 g of polymer product is added, with stirring, to this solution. The resultant material is filtered to remove the copolymer-copper complex and the filtrate, which is clear and colorless is tested for copper sulfate content. The filtrate analyzes less than 10 ppm CuSO<sub>4</sub>.

25           In another facet of the present invention, it has also been found that the "core monomers" disclosed in U.S. 5,362,843 can also be used in formulating new hyper-branched polymers. In this aspect, the branching monomer, end-capping monomer and core monomer are mixed together at a sufficient temperature and for a sufficient period of time to produce the desired polymer.

The core monomer used in this facet of the present invention includes the following seven categories of compounds (i.e. A-H):

A. dihydric phenol having the following formula:



5 wherein R is independently selected from hydrogen, an alkyl radical having from 1 to about 6 carbon atoms, preferably methyl, cycloalkyl having from 4 to about 7 carbon atoms, or aryl, Y is independently selected from alkyl groups of 1 to 4 carbon atoms, chlorine or bromine, z independently has a value of from 0 to 4, inclusive, and R' is independently selected from a  
10 having from 1 to 8 carbon atoms or halogenated derivatives thereof, especially  $C(CH_3)_2$ ,  $C(CX_3)_2$ ; wherein X is a halogen, preferably fluorine, cycloalkylene or cycloalkylidene radicals having up to and including 9 carbon atoms, halogenated derivatives thereof, O, S, SO,  $SO_2$ , CO; and x is 0 or 1.

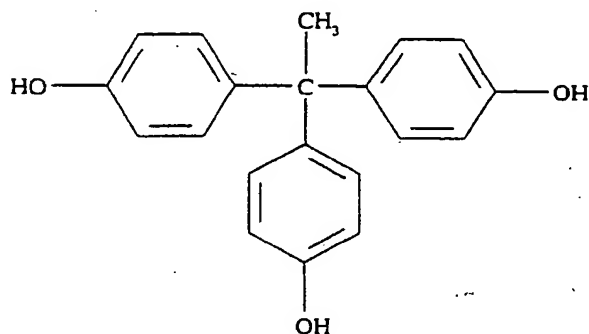
15 The dihydric phenols that may be used in this invention include but are not limited to the following:

2,2-bis-(4-hydroxyphenyl)propane,  
2,2-bis-(4-hydroxyphenyl)hexafluoropropane,  
bis-(2-hydroxyphenyl)methane,  
bis-(4-hydroxyphenyl)methane,  
20 bis-(4-hydroxy-2,6-dimethyl-3-methoxyphenyl)methane,  
1,1-bis-(4-hydroxyphenyl)ethane,  
1,2-bis-(4-hydroxyphenyl)ethane,  
1,1-bis-(4-hydroxy-2-chlorophenyl)ethane,  
1,1-bis-(3-methyl-4-hydroxyphenyl)ethane,  
25 1,3-bis-(3-methyl-4-hydroxyphenyl)propane,  
2,2-bis-(3-phenyl-4-hydroxyphenyl)propane,  
2,2-bis-(3-isopropyl-4-hydroxyphenyl)propane,

2,2-bis-(2-isopropyl-4-hydroxyphenyl)propane,  
2,2-bis-4-hydroxyphenyl)pentane,  
3,3-bis-(4-hydroxyphenyl)pentane,  
2,2-bis-(4-hydroxyphenyl)heptane,  
5 1,2-bis-(4-hydroxyphenyl)-1,2-bis-(phenyl)-propane,  
4,4'-(dihydroxyphenyl)ether,  
4,4'-(dihydroxyphenyl)sulfide,  
4,4'-(dihydroxyphenyl)sulfone,  
4,4'-(dihydroxyphenyl)sulfoxide,  
10 4,4'-(dihydroxybenzophenone),  
hydroquinone, and  
naphthalene diols.

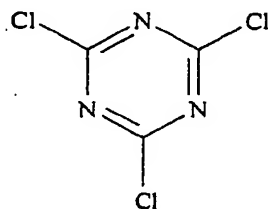
These dihydric phenols may be used individually or in any combination. It is also possible to add up to 50 wt. % based on the total diol content of aliphatic diols, such as  
15 neopentyl glycol. One common dihydric phenol is 2,2-bis(4-hydroxyphenyl)propane (bisphenol-A).

B.



(XVIII)

C.

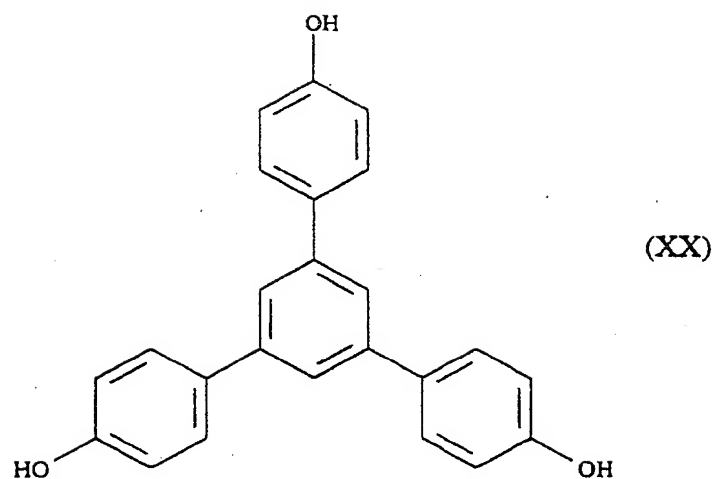


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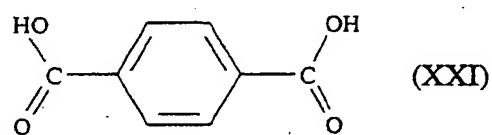
Cl can also be replaced with other halogens such as Br and F.

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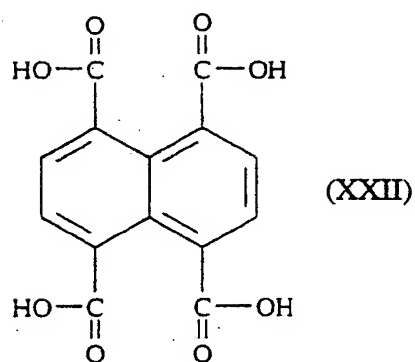
D.



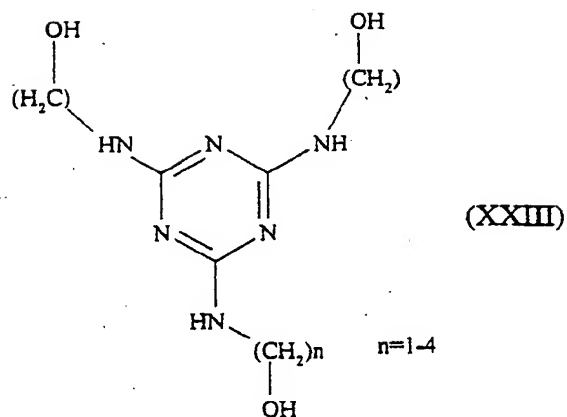
E.



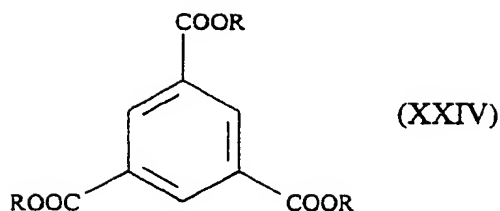
F.



5 G.



H.



where R is H, alkyl ( $C_1$ - $C_{20}$ ) and aromatic.

These hyperbranched polymers are prepared by first mixing and heating the branched monomer and core monomer together followed by the addition of end-capping monomer. In this 3 component system, the core monomer is used in the range of 0.001% by weight to about 20.0% by weight based on the weight of the 3 monomers combined.

The polymerization takes place under the same conditions as set forth herein as it pertains to the 2 component (i.e. branching monomer and end-capping monomer) system.

#### EXAMPLE 12

Polymerization of 3,5-Diacetoxybenzoic Acid with 1,1,1-Tris(4-Acetoxyphenyl)Ethane (THPE-Triacetate) as Monomer Core in Dowtherm A

3,5-Diacetoxybenzoic acid (9.67 g, 41 mmol), 1,1,1-tris(4-acetoxyphenyl)ethane (1 g, 2 mmol), Dowtherm A (100 g) and KOAc (0.01 g) were placed into a 3-neck round bottom flask fitted with a thermowell, mechanical stirrer, and distillation head. The Dowtherm A was used to help reduce the melt viscosity. The polymerization was conducted at 260°C for 2 hours. A brown solid was isolated by precipitating the dendrimer into MeOH. The brown solid was filtered and dried under vacuum.  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  168.93, 163.55, 162.67, 157.38, 151.22, 148.95, 146.48, 146.09, 131.66, 130.94, 130.76, 129.74, 128.77, 123.23, 121.30, 120.93, 116.88, 115.26, 51.59, 30.5, 20.84. The peaks at 166 and 115 in the  $^{13}\text{C}$  NMR indicate partial hydrolysis of the acetate end-groups.

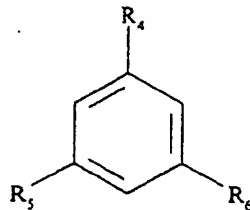
#### EXAMPLE 13

Two grams of the product (Example 12) is polymerized with 4 grams of end-capping monomer (Example 3) under the conditions of Example 12. The end product is light brown and NMR indicates the attachment of the end-capping monomer.

Although the invention has been illustrated by certain of the preceding examples, it is not to be construed as being limited thereby; but rather, the invention encompasses the generic area as hereinbefore disclosed. Various modifications and embodiments can be made without departing from the spirit and scope thereof.

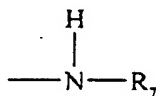
What is Claimed Is:

1. A composition of matter having the formula:



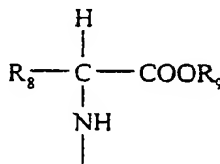
wherein  $R_4$  is selected from the group consisting of  $\text{COOR}$  wherein  $R$  is  $\text{H}$ , alkyl ( $\text{C}_1\text{-C}_{20}$ ) or aromatic;  $\text{C(O)-OC}_6\text{H}_5$ ;  $\text{O-CH}_2\text{CH}_2\text{OH}$ ;  $\text{O-C(O)-CH}_3$ ; and  $\text{N-CH}_2\text{CH}_2\text{OH}$ ;  $R_5$  and  $R_6$  are each independently selected from the group consisting of:

(A)



where  $R_7$  is a substituted or unsubstituted aryl or alkyl group;

(B)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group and  $R_9$  is  $\text{H}$  or alkyl;

(C)



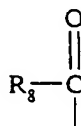
where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

(D)



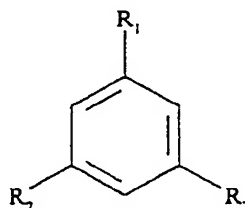
where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

(E)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group; and

- (F) chiral or racemic phosphine ligands.
2. The composition as set forth in claim 1 wherein  $R_5$  and  $R_6$  are (A).
  3. The composition as set forth in claim 1 wherein  $R_5$  and  $R_6$  are (B).
  4. The composition as set forth in claim 1 wherein  $R_5$  and  $R_6$  are (C).
  5. The composition as set forth in claim 1 wherein  $R_5$  and  $R_6$  are (D).
  6. The composition as set forth in claim 1 wherein  $R_5$  and  $R_6$  are (E).
  7. The composition as set forth in claim 1 wherein  $R_5$  and  $R_6$  are (F).
  8. The composition as set forth in claim 1 wherein  $R_4$  is COOR.
  9. The composition as set forth in claim 1 wherein there is at least one chiral carbon center.
  10. The composition as set forth in claim 1 wherein there are at least two chiral carbon centers.
  11. The composition as set forth in claim 1 wherein there are no chiral carbon centers.
  12. The composition of any of the preceeding claims used in engineering resins, fiber, film, bottle resins, rheology modifiers, drug delivery systems, membranes, chelating agents, and catalyst support.
  13. The composition of any of claims 1-11, incorporated or copolymerized with polysulfone and/or polycarbonate polymers.
  14. A process for preparing a highly branched macromolecule polymer comprising the step of reacting a branching monomer, having functional groups thereon, having the formula:



wherein  $R_1$  is independently selected from the group consisting of:

COOR where R is H, alkyl ( $C_1$ - $C_{20}$ ) or aromatic;

$C(O) - OC_6H_5$ ;

$O - CH_2CH_2OH$ ;

$O - C(O) - CH_3$ , and

$N - CH_2CH_2OH$ ;



$R_2$  and  $R_3$  are each independently selected from the group consisting of:

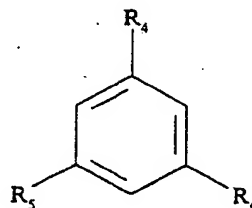
COOR where R is H, alkyl ( $C_1$ - $C_{20}$ ) or aromatic;

OH;

$NH_2$ ; and

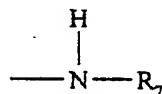
O - C(O) -  $CH_3$ ;

with the proviso that (a) when  $R_1$  is -COOR,  $R_2$  and  $R_3$  must be the same but not equal to  $R_1$ , and  $R_2$  and  $R_3$  are either OH or O-C(O)- $CH_3$ , and (b) when  $R_1$  is -C(O)- $OC_6H_5$ ,  $R_2$  and  $R_3$  are equal and are either OH or  $NH_2$ ; and (c) when  $R_1$  is O- $CH_2CH_2OH$ ,  $R_2$  and  $R_3$  are equal, and  $R_2$  and  $R_3$  are COOR; with a end-capping monomer having the formula:



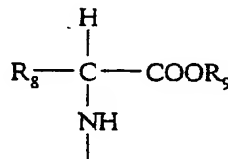
wherein  $R_4$  is selected from the group consisting of COOR wherein R is H, alkyl ( $C_1$ - $C_{20}$ ) or aromatic; C(O)- $OC_6H_5$ ; O- $CH_2CH_2OH$ ; O-C(O)- $CH_3$ ; and N- $CH_2CH_2OH$ ;  $R_5$  and  $R_6$  are each independently selected from the group consisting of:

(A)



where  $R_7$  is a substituted or unsubstituted aryl or alkyl group;

(B)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group and  $R_9$  is H or alkyl;

(C)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

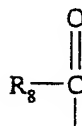
32

(D)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

(E)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group; and

(F) chiral or racemic phosphine ligands, at a temperature of at least about 25°C and for a period of time to produce said highly branched polymer;

with the proviso that, in the above terms, alkyl means  $C_1$ - $C_{20}$ ; aryl means phenyl and naphthyl; aromatic means substituted and unsubstituted phenyl and naphthyl; and heterocyclic means a 5 to 10 membered mono- or fused-ring system containing carbon and nitrogen, oxygen, and/or sulfur.

15. The process as set forth in claim 14 wherein the temperature is from about 25°C to about 275°C.

16. The process as set forth in claim 15 wherein there is included an inert diluent in the reaction.

17. The process as set forth in claim 14 wherein  $R_1$  is  $O-C(O)-CH_3$ .

18. The process as set forth in claim 14 wherein  $R_2$  and  $R_3$  are both  $COOH$ .

19. The process as set forth in claim 14 wherein  $R_5$  and  $R_6$  are both (A).

20. The process as set forth in claim 14 wherein  $R_5$  and  $R_6$  are both (B).

21. The process as set forth in claim 14 wherein  $R_5$  and  $R_6$  are both (C).

22. The process as set forth in claim 14 wherein  $R_4$  is  $O-C(O)-CH_3$ .

23. The process as set forth in claim 16 wherein there is additionally included a suitable catalyst which promotes the reaction between said monomer and said end-capping monomer.

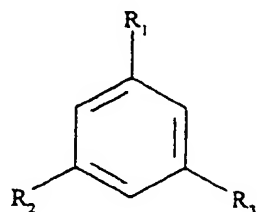
24. The process as set forth in claim 23 wherein the catalyst is lithium acetate.

25. The product produced by the process of any of claims 14-24.

26. The process as set forth in claim 14 wherein the end-capping monomer has at least one chiral carbon center.

27. The process as set forth in claim 14 wherein the end-capping monomer has at least two chiral carbon centers.

28. A process for preparing a highly branched macromolecule polymer comprising the step of reacting (i) a branching monomer, having functional groups thereon, having the formula:



wherein  $\text{R}_1$  is independently selected from the group consisting of:

$\text{COOR}$  where  $\text{R}$  is  $\text{H}$ , alkyl ( $\text{C}_1\text{-C}_{20}$ ) or aromatic;

$\text{C(O) - OC}_6\text{H}_5$ ;

$\text{O - CH}_2\text{CH}_2\text{OH}$ ;

$\text{O - C(O) - CH}_3$ ; and

$\text{N - CH}_2\text{CH}_2\text{OH}$ ;

$\text{R}_2$  and  $\text{R}_3$  are each independently selected from the group consisting of:

$\text{COOR}$  where  $\text{R}$  is  $\text{H}$ , alkyl ( $\text{C}_1\text{-C}_{20}$ ) or aromatic;

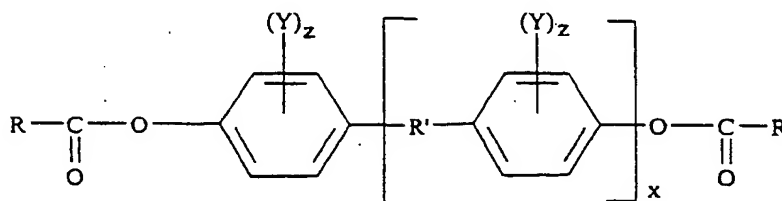
$\text{OH}$ ;

$\text{NH}_2$ ; and

$\text{O - C(O) - CH}_3$ ;

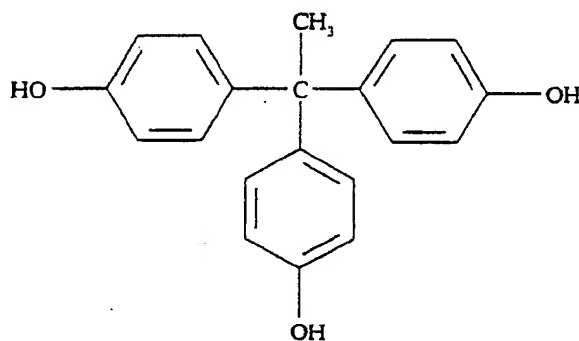
with the proviso that (a) when  $\text{R}_1$  is  $-\text{COOR}$ ,  $\text{R}_2$  and  $\text{R}_3$  must be the same but not equal to  $\text{R}_1$ , and  $\text{R}_2$  and  $\text{R}_3$  are either  $\text{OH}$  or  $\text{O-C(O)-CH}_3$ , and (b) when  $\text{R}_1$  is  $-\text{C(O)-OC}_6\text{H}_5$ ,  $\text{R}_2$  and  $\text{R}_3$  are equal and are either  $\text{OH}$  or  $\text{NH}_2$ ; and (c) when  $\text{R}_1$  is  $\text{O-CH}_2\text{CH}_2\text{OH}$ ,  $\text{R}_2$  and  $\text{R}_3$  are equal, and  $\text{R}_2$  and  $\text{R}_3$  are  $\text{COOR}$ ; (ii) a core monomer, having functional groups thereon, selected from the group consisting of:

(I)

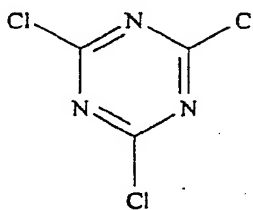


wherein R is independently selected from the group consisting of hydrogen, an alkyl radical having from 1 to 6 carbon atoms, cycloalkyl having from 4 to 7 carbon atoms, and aryl, Y is independently selected from the group consisting of an alkyl group of 1 to 4 carbon atoms, chlorine and bromine, z independently has a value of 0 to 4, inclusive, R<sub>1</sub> is independently selected from the group consisting of 1 to 8 carbon atoms and halogenated derivatives thereof, cycloalkylene or cycloalkylidene radicals having up to and including 9 carbon atoms and halogenated derivatives thereof, O, S, SO, SO<sub>2</sub>, and CO; and x is 0 or 1;

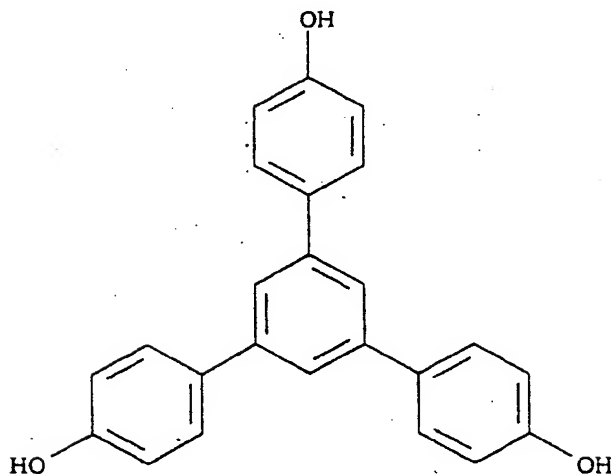
(II)



(III)

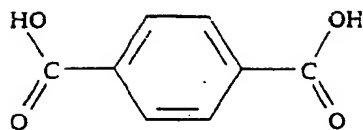


(IV)

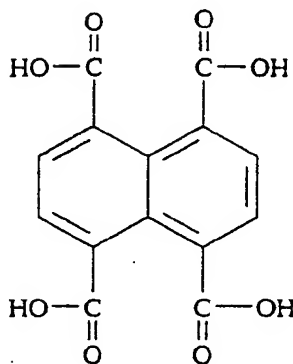


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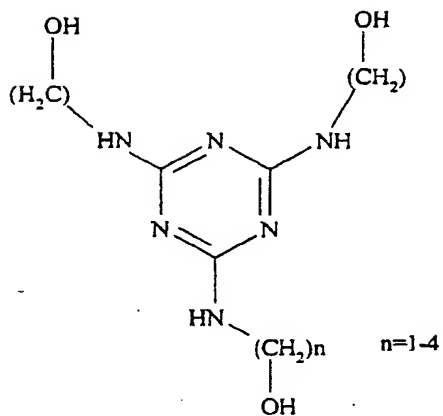
(V)



(VI)

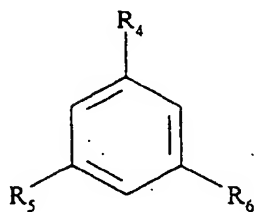


(VII)



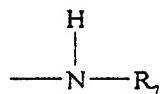
and

(iii) an end-capping monomer having the formula:



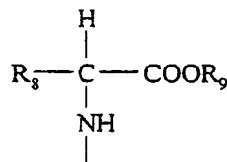
wherein  $R_4$  is selected from the group consisting of COOR wherein R is H, alkyl ( $C_1$ - $C_{20}$ ) or aromatic;  $C(O)-OC_6H_5$ ;  $O-CH_2CH_2OH$ ;  $O-C(O)-CH_3$ ; and  $N-CH_2CH_2OH$ ;  $R_5$  and  $R_6$  are each independently selected from the group consisting of:

(A)



where  $R_7$  is a substituted or unsubstituted aryl or alkyl group;

(B)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group and  $R_9$  is H or alkyl;

(C)



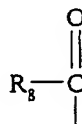
where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

(D)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group;

(E)



where  $R_8$  is a substituted or unsubstituted heterocyclic, aryl, or alkyl group; and

(F) chiral or racemic phosphine ligands, at a sufficient temperature and for a sufficient period of time to produce said highly branched polymer.

29. The process as set forth in claim 28 wherein the temperature is at least 25°C.

30. The process as set forth in claim 28 wherein the temperature is from about 25°C to about 275°C.

31. The process as set forth in claim 30 wherein there is included an inert diluent in the reaction.
32. The process as set forth in claim 28 wherein  $R_1$  is  $O-C(O)-CH_3$ .
33. The process as set forth in claim 28 wherein  $R_2$  and  $R_3$  are both  $COOH$ .
34. The process as set forth in claim 28 wherein  $R_5$  and  $R_6$  are both respectively (A), or both respectively (B), or both respectively (C).
35. The process as set forth in claim 28 wherein  $R_4$  is  $O-C(O)-CH_3$ .
36. The process as set forth in claim 31 wherein there is additionally included a suitable catalyst which promotes the reaction.
37. The process as set forth in claim 36 wherein the catalyst is lithium acetate.
38. The product produced by the process of any of claims 28-37.
39. The process as set forth in claim 28 wherein the end-capping monomer has at least one chiral carbon center.
40. The process as set forth in claim 28 wherein the end-capping monomer has at least two chiral carbon centers.

# INTERNATIONAL SEARCH REPORT

International Application No  
PC 1/US 96/13341

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K47/48 C08G63/00 C07D209/20 C07C235/52

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 28, no. 1, 10 January 1934 Columbus, Ohio, US; MADHAVAL S. SHAH ET ALL.: "Thiols derived from o-,m-,p-methoxytoluenes and benzoic acid" column 124; XP002021735 see abstract & JOURNAL OF THE CHEMICAL SOCIETY, 1933, LETCHWORTH GB, pages 1375-1381, --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

19 December 1996

Date of mailing of the international search report

06.01.97

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# INTERNATIONAL SEARCH REPORT

International Application No  
PC./US 96/13341

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 24, no. 7, 10 April 1930 Columbus, Ohio, US; ERNEST V. BELL ET ALL.: "Stereoisomerism of disulfoxides and related substances. V. The dioxides of 3,5-dimethylthiolbenzoic acid." page 1857; XP002021736 see abstract & JOURNAL OF THE CHEMICAL SOCIETY, 1930, LETCHWORTH GB, pages 1-6,	1,5
X	--- TETRAHEDRON, (INCL TETRAHEDRON REPORTS), vol. 19, 1963, OXFORD GB, pages 111-115, XP002021732 A.KAMAL ET ALL.: "Studies in the biochemistry of micro-organisme-II" see page 111, paragraph 8 - page 112, paragraph 1	1,4
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